A MODERN APPROACH TO ORGANIC CHEMISTRY

BY

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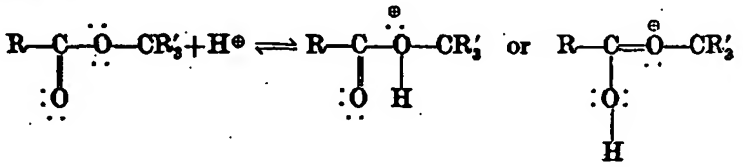
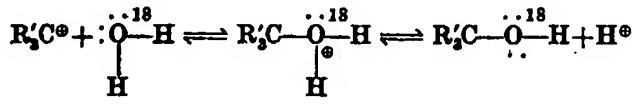
carbon atom) in which the carbonyl group takes no direct part.† It seems reasonable to assume, as has been done throughout this chapter, that other reactions of the carbonyl group and of its derived groups (e.g. ester, acid chloride, amide, and anhydride groups) also proceed by way of an intermediate addition product unless they occur by a unimolecular mechanism (see p. 272).

There is indirect evidence that in the acid hydrolysis of the esters of *tertiary* alcohols, alkyl-oxygen fission occurs (Kenyon and Phillips, 1936; Cohen and Schneider, 1941). This has now been confirmed by a study of the acid hydrolysis of *tert*-butyl acetate in water enriched with O^{18}. The *tert*-butyl alcohol formed was found to be enriched in the O^{18} tracer (Bunton, Comyns, and Wood, 1951). The mechanism suggested is:



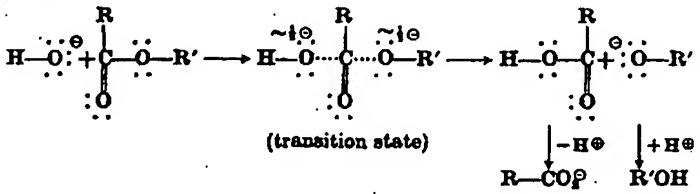
$$\rightleftharpoons R{-}CO_2H + {}^{\oplus}CR'_3$$



When the hydrolysis of an ester is carried out with sodium or potassium hydroxide solution, the sodium or potassium salt of the acid is obtained. Since these salts of long-chain acids (from fats and oils) are soaps, alkaline hydrolysis is frequently referred to as saponification (meaning soap formation), even though the salts of the lower acids of short chain lengths are not soaps.

Alcoholysis. Esters react reversibly with alcohols in the presence of a small amount of a strong acid or sodium alkoxide as catalyst. The reaction is the equivalent of hydrolysis with water under acid or alkaline

† Such a mechanism could be formulated as follows (e.g. for alkaline hydrolysis of an ester):



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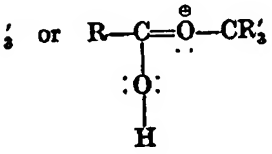

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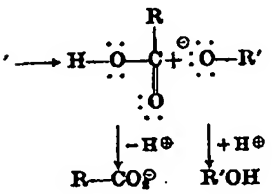


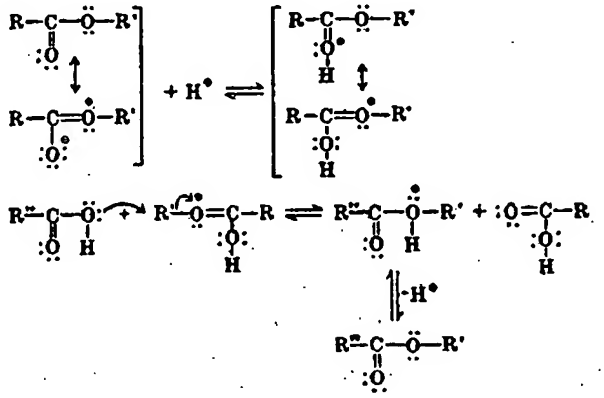
conditions and the mechanisms are no doubt similar. The overall result is:

$$R{-}CO.OR' + R''OH \rightleftharpoons R{-}CO.OR'' + R'OH$$

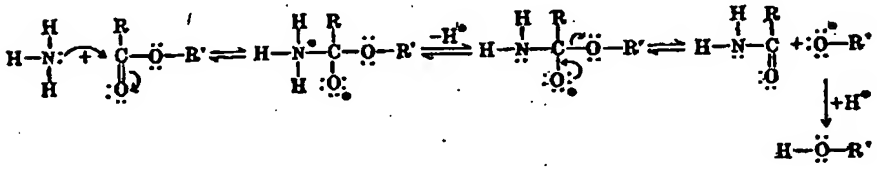
Acidolysis. Esters also react reversibly with carboxylic acids in the presence of a strong acid as catalyst:

$$R.COOR' + R''.CO_2H \rightleftharpoons R''.COOR' + R.CO_2H$$

This appears to be a nucleophilic substitution on the carbon atom of the 'alcoholic' alkyl group in the protonated ester:



Ammonolysis. Ammonia reacts with esters to form amides:



This reaction can often be carried out by shaking together the ester and concentrated aqueous (0·880) ammonia solution, and it is a common laboratory preparative method. When the reaction is too slow with aqueous ammonia, it can usually be carried out successfully with anhydrous liquid ammonia. Hydroxylamine and hydrazine also react with esters in a similar way to give hydroxamic acids and hydrazides respectively (see reaction with acyl chlorides, p. 273).

With Grignard reagents. Grignard reagents react with esters to give tertiary alcohols, the alkoxyl group being eliminated in the process.